

Identifiability and parameter estimation of the single particle lithium-ion battery model

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Abstract

This paper investigates the identifiability and estimation of the parameters of the single particle model (SPM) for lithium-ion battery simulation. Identifiability is addressed both in principle and in practice. The approach begins by grouping parameters and partially non-dimensionalising the SPM in order to understand the maximum expected degrees of freedom in the problem. We discover that, excluding open circuit voltage, there are only six unique parameters in the model. We then examine the structural identifiability by asking whether the transfer function of the linearised SPM is unique. It is found that the model is unique provided that the electrode open circuit voltage functions have a known and non-zero gradient, the parameters are ordered, and that the behaviour of the kinetics of each electrode is lumped together into a single parameter which is the charge transfer resistance. We then run simulations to demonstrate the practical estimation of parameters from noisy data.

Keywords: lithium-ion battery, structural identifiability, parameter estimation

1. Introduction

The importance of lithium-ion batteries in automotive, off-grid and grid power applications is increasing, in addition to their widespread use in consumer electronics. In order to improve the performance of a battery pack, researchers are investigating the application of electrochemical models in the battery management system (BMS), for example to enable electrochemical control of fast charging [1, 2, 3]. This is a challenging research area both from the modelling and numerical solution perspective, but also the application perspective. One key challenge is whether such models are observable and can be used for state estimation. Recent promising results indicate that electrochemical models could indeed be

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used in this way [4, 5, 6, 7, 8, 9, 10, 11]. However, another important condition for the use of an electrochemical model in a BMS is that the parameters of the model must be credibly obtained. In general, parameters in these models are obtained from the literature (for example [12, 10]), and whilst this is useful for initial design studies of cell performance in various applications, for use in a BMS, the model must be parameterised specifically for the cells used in the pack. Relatively few authors have tackled this parameter estimation problem [13, 14, 15, 16, 17] although it has been investigated in the context of equivalent circuit models of battery dynamics [18, 19, 20, 21].

In this paper we investigate the parameter estimation challenge in a simplified version of the ‘Doyle-Fuller-Newman’ pseudo-two-dimensional lithium-ion battery model [22], the so-called single particle model (SPM) [23, 24], first to see whether groups of parameters are identifiable in principle, and then to investigate whether in practice they can be identified from simulated data.

2. The single-particle model

2.1. Spherical particle diffusion model

In the single particle model (SPM), first introduced by [23] and later extended to lithium-ion batteries by [24], the diffusion of lithium in the active material of each battery electrode i (anode or cathode) is governed by the Fickian diffusion equation in spherical coordinates

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial c_i}{\partial r_i} \right), \quad (1)$$

where r_i denotes the radial coordinates, c_i the lithium concentration profile and D_i the lithium diffusion coefficient (assumed uniform) in electrode i . The subscript i either takes the value + or – to refer to the cathode or anode domain respectively. The diffusion equation is subject to Neumann boundary conditions at the particle centre $r_i = 0$ and surface $r_i = R_i$,

$$\left. \frac{\partial c_i}{\partial r_i} \right|_{r_i=0} = 0 \quad \text{and} \quad D_i \left. \frac{\partial c_i}{\partial r_i} \right|_{r_i=R_i} = -j_i, \quad (2)$$

and the initial condition equation,

$$c_i(0, r_i) = c_i^0, \quad (3)$$

where c_i^0 is the initial concentration profile in each particle. The molar flux j_i in (2) expresses the rate of the lithium intercalation/de-intercalation reaction. In contrast to the Doyle–Fuller–Newman model [22] where algebraic equations must be solved to obtain the molar flux for each particle, the molar fluxes in the SPM can be directly related to the applied battery current I through the relationships,

$$j_- = \frac{+I}{a_- \delta_- \mathcal{F} \mathcal{A}} \quad \text{and} \quad j_+ = \frac{-I}{a_+ \delta_+ \mathcal{F} \mathcal{A}}, \quad (4)$$

where $a_i = 3\epsilon_i/R_i$ is the specific active surface area in electrode i , ϵ_i is the volume fraction of active material in an electrode, \mathcal{F} is Faraday’s constant, \mathcal{A} is the electrode surface area which

is assumed equal for both electrodes, and δ_i is the thickness of the electrode i . By convention, the battery discharge current is positive and the charging current is negative. These molar flux expressions also assume an electrochemical reaction involving a single electron transfer, which is the case for the lithium intercalation/de-intercalation reaction.

2.2. Voltage measurement equation

The initial-boundary value problems (1)-(2)-(3) for each electrode constitute the dynamic part of the single-particle model. The battery terminal voltage V is given by the nonlinear measurement equation,

$$V = U_+(x_+^s) - U_-(x_-^s) + \eta_+ - \eta_-. \quad (5)$$

The anode and cathode open-circuit potential (OCP) U_- and U_+ respectively are empirical nonlinear functions of the surface stoichiometry of each particle $x_i^s = c_i^s/c_i^{max}$. The overpotential η_i is the voltage drop due to the departure from equilibrium potential associated with the intercalation/de-intercalation reaction in each electrode. The relationship between the reaction rate j_i and the overpotential η_i is given by the Butler-Volmer kinetics equation

$$j_i = \frac{i_{0,i}}{\mathcal{F}} \left(\exp\left(\frac{\alpha_{a,i}\mathcal{F}}{RT}\eta_i\right) - \exp\left(\frac{-\alpha_{c,i}\mathcal{F}}{RT}\eta_i\right) \right). \quad (6)$$

The exchange current density $i_{0,i}$ depends on the reaction rate constant k_i and the reactants and products concentrations, i.e. the electrolyte concentration c_e (assumed constant in this model), and the lithium solid-phase concentration c_i^s at the surface of the particle, through the relation

$$i_{0,i} = k_i \mathcal{F} \sqrt{c_e} \sqrt{c_i^s} \sqrt{c_i^{max} - c_i^s}. \quad (7)$$

By assuming that the anodic and cathodic charge transfer coefficients in (6) are equal $\alpha_{a,i} = \alpha_{c,i} = 0.5$, the overpotential η_i can be expressed as a function of the reaction rate j_i by

$$\eta_i = \frac{2RT}{\mathcal{F}} \sinh^{-1} \left(\frac{j_i \mathcal{F}}{2i_{0,i}} \right). \quad (8)$$

2.3. Identification of grouped parameters

First-principle models, such as the SPM, are usually over-parametrised in the sense that only a subset of parameters can be estimated from measured input-output data. A first necessary step towards credible parameter estimation is to reformulate the model in terms of the minimum number of parameter groups. In order to identify such groups of parameters, we first introduce the dimensionless radial coordinates $\bar{r} = r_i/R_i$, and the stoichiometry $x_i = c_i/c_i^{max}$, instead of the concentration in the governing equations. In addition, the change of variable $\bar{x}_i = x_i - x_i^0$ is introduced, with $x_i^0 = c_i^0/c_i^{max}$ being the initial stoichiometry in each particle i , in order to set the initial condition to zero in the governing equations. Note the time independent variable t is kept dimensional because the diffusion time constants are different in each electrode. Introducing these dimensionless variables, the initial-boundary value problem (1)-(2)-(3) can be written equivalently

$$\frac{\partial \bar{x}_i}{\partial t} = \frac{D_i}{R_i^2} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left(\bar{r}^2 \frac{\partial \bar{x}_i}{\partial \bar{r}} \right), \quad (9)$$

subject to the boundary conditions

$$\left. \frac{\partial \bar{x}_i}{\partial \bar{r}} \right|_{\bar{r}=0} = 0 \quad \text{and} \quad \left. \frac{\partial \bar{x}_i}{\partial \bar{r}} \right|_{\bar{r}=1} = \frac{-R_i}{D_i c_i^{max}} j_i, \quad (10)$$

with initial conditions

$$\bar{x}_i(0, \bar{r}) = 0. \quad (11)$$

The boundary condition at the surface of the particle in each electrode can also be written in terms of the input current I instead of the fluxes j_i using relations (4) according to

$$\left. \frac{\partial \bar{x}_+}{\partial \bar{r}} \right|_{\bar{r}=1} = + \frac{R_+^2}{D_+} \frac{I}{3\epsilon_+ \delta_+ c_+^{max} \mathcal{F} \mathcal{A}} \quad (12)$$

$$\left. \frac{\partial \bar{x}_-}{\partial \bar{r}} \right|_{\bar{r}=1} = - \frac{R_-^2}{D_-} \frac{I}{3\epsilon_- \delta_- c_-^{max} \mathcal{F} \mathcal{A}}. \quad (13)$$

Similarly using relation (4) the expression for the overpotential in each electrode (8) becomes

$$\eta_+ = \frac{2RT}{\mathcal{F}} \sinh^{-1} \left(- \frac{R_+}{2k_+ \sqrt{c_e}} \frac{1}{3\epsilon_+ \delta_+ c_+^{max} \mathcal{F} \mathcal{A}} \frac{I}{\sqrt{x_+^s (1 - x_+^s)}} \right) \quad (14)$$

$$\eta_- = \frac{2RT}{\mathcal{F}} \sinh^{-1} \left(+ \frac{R_-}{2k_- \sqrt{c_e}} \frac{1}{3\epsilon_- \delta_- c_-^{max} \mathcal{F} \mathcal{A}} \frac{I}{\sqrt{x_-^s (1 - x_-^s)}} \right) \quad (15)$$

with the the voltage measurement (5) expression unchanged. Six physically meaningful groups of parameters naturally arise in these equations. Indeed one can identify three groups of parameters for each electrode: a diffusion time constant τ_i^d , kinetics time constant τ_i^k and the maximum theoretical electrode capacity Q_i^{th} . The expressions for these six physically meaningful groups of parameters are defined as follows

$$\tau_+^d = \frac{R_+^2}{D_+} \quad \tau_-^d = \frac{R_-^2}{D_-} \quad (16)$$

$$\tau_+^k = \frac{R_+}{2k_+ \sqrt{c_e}} \quad \tau_-^k = \frac{R_-}{2k_- \sqrt{c_e}} \quad (17)$$

$$Q_+^{th} = -\epsilon_+ \delta_+ c_+^{max} \mathcal{F} \mathcal{A} \quad Q_-^{th} = +\epsilon_- \delta_- c_-^{max} \mathcal{F} \mathcal{A} \quad (18)$$

Note that for convenience the cathode theoretical capacity Q_+^{th} is defined negative to yield the same model structure in both the anode and cathode. Substituting these grouped parameters into the governing equations result in the following diffusion equation for both the cathode and anode

$$\frac{\partial \bar{x}_i}{\partial t} = \frac{1}{\tau_i^d} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left(\bar{r}^2 \frac{\partial \bar{x}_i}{\partial \bar{r}} \right) \quad (19)$$

subject to the boundary conditions

$$\left. \frac{\partial \bar{x}_i}{\partial \bar{r}} \right|_{\bar{r}=0} = 0 \quad \text{and} \quad \left. \frac{\partial \bar{x}_i}{\partial \bar{r}} \right|_{\bar{r}=1} = - \frac{\tau_i^d}{3Q_i^{th}} I \quad (20)$$

with initial condition

$$\bar{x}_i(0, \bar{r}) = 0. \quad (21)$$

The voltage measurement equation remains

$$V = U_+(x_+^s) - U_-(x_-^s) + \eta_+ - \eta_-, \quad (22)$$

with the cathode and anode overpotentials given by

$$\eta_+ = \frac{2RT}{F} \sinh^{-1} \left(\frac{\tau_+^k}{3Q_+^{th}} \frac{I}{\sqrt{x_+^s(1-x_+^s)}} \right) \quad (23)$$

$$\eta_- = \frac{2RT}{F} \sinh^{-1} \left(\frac{\tau_-^k}{3Q_-^{th}} \frac{I}{\sqrt{x_-^s(1-x_-^s)}} \right). \quad (24)$$

Inspecting (19) through (24) one can identify six groups of parameters θ_i that fully parametrise the SPM given by the parameter vector $\boldsymbol{\theta} \in \mathbb{R}^6$:

$$\boldsymbol{\theta} = \left[\tau_+^d \quad \frac{\tau_+^d}{3Q_+^{th}} \quad \frac{\tau_+^k}{3Q_+^{th}} \quad \tau_-^d \quad \frac{\tau_-^d}{3Q_-^{th}} \quad \frac{\tau_-^k}{3Q_-^{th}} \right]^T. \quad (25)$$

Unlike the parameters defined in (16)–(17)–(18), these parameters θ_i appear only once and not as a product of each other in the model equations. Moreover, one can show that there is a one-to-one mapping between the six parameter θ_i and the six parameters (16)–(17)–(18) defined by:

$$\begin{cases} \tau_+^d &= \theta_1 \\ \tau_+^k &= (\theta_1 \theta_3) / \theta_2 \\ Q_+^{th} &= \theta_1 / (3\theta_2) \\ \tau_-^d &= \theta_4 \\ \tau_-^k &= (\theta_4 \theta_6) / \theta_5 \\ Q_-^{th} &= \theta_4 / (3\theta_5) \end{cases} \quad (26)$$

Therefore, assuming that the initial electrode stoichiometries x_i^0 (i.e. state-of-charge) are known and that the open-circuit potentials are known functions of the surface stoichiometry for each electrode, the six parameters contained in $\boldsymbol{\theta}$, or equivalently the six parameters defined in (16–18), are sufficient to fully parametrise the single-particle model.

3. Structural identifiability

A set of six grouped parameters has been identified as sufficient to fully parametrise the single-particle model. However, this does not imply that these six parameters can be mathematically identified from the battery current-voltage response. Several approaches can be used to investigate the parameter identifiability of a dynamical model from input-output data. In this section, the so-called *structural identifiability* [25] of the single-particle model

is discussed. Structural identifiability investigates the mathematical identifiability of the model irrespective of the identification data considered (which are also assumed noise-free). A definition of structural identifiability for linear time-invariant dynamic models that can be cast into a transfer function $H(s, \boldsymbol{\theta})$ parametrised by a vector of parameters $\boldsymbol{\theta}$ is given as follows [26, 27].

Definition 1. *Consider a model structure \mathcal{M} with the transfer function $H(s, \boldsymbol{\theta})$ parametrised by $\boldsymbol{\theta} \in \mathcal{D} \subset \mathbb{R}^n$ where n denotes the number of parameters of the model. The identifiability equation for \mathcal{M} is given by*

$$H(s, \boldsymbol{\theta}) = H(s, \boldsymbol{\theta}^*) \quad \text{for almost all } s, \quad (27)$$

where $\boldsymbol{\theta}, \boldsymbol{\theta}^* \in \mathcal{D}$. The model structure \mathcal{M} is said to be

- globally identifiable if (27) has a unique solution in \mathcal{D} ,
- locally identifiable if (27) has a finite number of solutions in \mathcal{D} ,
- unidentifiable if (27) has a infinite number of solutions in \mathcal{D} .

The SPM is not a linear dynamical model because of its voltage measurement equation (22) incorporating nonlinear Butler-Volmer kinetics (23,24), and nonlinear OCP functions. Therefore Definition 1 cannot directly be used to investigate the SPM structural identifiability unless we first linearise the model by assuming a small perturbation around a fixed depth-of-discharge (DoD) point. Since we assume the nonlinear OCP functions are measured and known a priori (for example using the techniques described in [28, 29]), linearisation is a valid approach to obtain the parameters of the diffusion sub-models, which are linear, and to obtain a linearised approximation of the kinetics. The subject of identifiability and parameter estimation of the nonlinear kinetics term in the output equation would be an interesting topic for further research.

3.1. Diffusion model transcendental transfer function

Definition 1 requires the model transfer function; we therefore first derive this for the spherical particle diffusion model and then combine it in subsequent sections with the transfer function of the linearised voltage measurement equation to derive the transfer function for the linearised SPM. In order to simplify the derivation of the diffusion model transfer function, the change of variable $\bar{u}_i = \bar{r}\bar{x}_i$ is introduced into the initial-boundary value problem (19)–(20)–(21) describing the diffusion in a spherical particle. Under this change of variable (19) can be equivalently written

$$\frac{\partial \bar{u}_i}{\partial t} = \frac{1}{\tau_i^d} \frac{\partial^2 \bar{u}_i}{\partial \bar{r}^2}, \quad (28)$$

and the boundary conditions (20) become

$$\bar{u}_i(r_i = 0) = 0 \quad \text{and} \quad \left. \frac{\partial \bar{u}_i}{\partial \bar{r}} \right|_{\bar{r}=1} - u(\bar{r} = 1) = \frac{-\tau_i^d}{3Q_i^{th}} I. \quad (29)$$

Note that the homogeneous Neumann boundary condition at the centre of the particle can be reduced to a simpler homogeneous Dirichlet boundary condition so that $\lim_{r_i \rightarrow 0} c_i(r_i)$ remains finite. By introducing this change of variable the initial condition (3) conveniently becomes

$$\bar{u}_i(0, \bar{r}) = 0. \quad (30)$$

Since the initial-boundary value diffusion problem (28)–(29)–(30) is linear, an equivalent transfer function can be determined without loss of generality. Taking the Laplace transform of (28) yields

$$\frac{d^2 \bar{U}_i(s, \bar{r})}{d\bar{r}^2} - s\tau_i^d \bar{U}_i(s, \bar{r}) = 0 \quad (31)$$

where s is the frequency-domain Laplace variable. The characteristic equation for this differential equation is

$$\lambda^2 - s\tau_i^d = 0 \quad \Rightarrow \quad \lambda = \pm \sqrt{s\tau_i^d}, \quad (32)$$

and its general solution is therefore

$$\bar{U}_i(s, \bar{r}) = A_i(s)e^{+\bar{r}\sqrt{s\tau_i^d}} + B_i(s)e^{-\bar{r}\sqrt{s\tau_i^d}} \quad (33)$$

with $A_i(s)$, $B_i(s)$ two constants (with respect to \bar{r}) to be determined using the boundary conditions (29). Substituting (33) into the particle centre boundary condition (29) at $\bar{r} = 0$ yields

$$B_i(s) = -A_i(s). \quad (34)$$

And substituting (33) and (34) into the surface boundary conditions (29) at $\bar{r} = 1$ yields

$$A_i(s) = \frac{\tau_i^d}{3Q_i^{th}} \frac{I(s)/2}{\sinh(\sqrt{s\tau_i^d}) - \sqrt{s\tau_i^d} \cosh(\sqrt{s\tau_i^d})} \quad (35)$$

Substituting (35)–(34) into (33) yields the general solution for $\bar{U}_i(s, \bar{r})$

$$\bar{U}_i(s, \bar{r}) = \frac{\tau_i^d}{3Q_i^{th}} \frac{\sinh(\bar{r}\sqrt{s\tau_i^d})}{\sinh(\sqrt{s\tau_i^d}) - \sqrt{s\tau_i^d} \cosh(\sqrt{s\tau_i^d})} I(s) \quad (36)$$

The variable of interest is the surface stoichiometry $\bar{X}_i^s(s)$, rather than $\bar{U}_i(s, \bar{r})$, since this is the variable involved in the voltage measurement equation. By substituting $\bar{u}_i = \bar{r}\bar{x}_i$ into (36), evaluating at $\bar{r} = 1$ and dividing by the input current $I(s)$, the transfer function $H_i^d(s)$ for the spherical diffusion model is given by

$$H_i^d(s) = \frac{\bar{X}_i^s(s)}{I(s)} = \frac{\tau_i^d}{3Q_i^{th}} \frac{\tanh(\sqrt{s\tau_i^d})}{\tanh(\sqrt{s\tau_i^d}) - \sqrt{s\tau_i^d}}. \quad (37)$$

The cathode and anode diffusion transfer functions expressed in terms of the parameter vector $\boldsymbol{\theta}$ are therefore respectively

$$H_+^d(s, \boldsymbol{\theta}) = \frac{\theta_2 \tanh(\sqrt{s\theta_1})}{\tanh(\sqrt{s\theta_1}) - \sqrt{s\theta_1}}, \quad (38)$$

and

$$H_-^d(s, \boldsymbol{\theta}) = \frac{\theta_5 \tanh(\sqrt{s\theta_4})}{\tanh(\sqrt{s\theta_4}) - \sqrt{s\theta_4}}. \quad (39)$$

3.2. Linearisation of the voltage measurement equation

The voltage measurement equation is a nonlinear function of the anode and cathode surface stoichiometry x_-^s and x_+^s respectively, and the input current I . Assuming that the input current amplitude I remains small and that the battery is operated close to its initial DoD, i.e. the stoichiometry in both electrodes remains close to the initial value x_i^0 , the voltage equation can be linearised using a first-order Taylor series approximation about the reference point $\mathbf{x}_0 = (x_+^0, x_-^0, I_0 = 0)$ according to

$$V \approx V(\mathbf{x}_0) + \left. \frac{\partial V}{\partial x_+^s} \right|_{\mathbf{x}_0} \bar{x}_+^s + \left. \frac{\partial V}{\partial x_-^s} \right|_{\mathbf{x}_0} \bar{x}_-^s + \left. \frac{\partial V}{\partial I} \right|_{\mathbf{x}_0} I, \quad (40)$$

where

$$V(\mathbf{x}_0) = U_+(x_+^0) - U_-(x_-^0) \quad (41)$$

is the equilibrium voltage of the battery at the DoD linearisation point. Defining the deviation of the voltage from the equilibrium voltage at the linearisation point $\bar{V}^0 = V - V(\mathbf{x}_0)$ which is given by the linear approximation

$$\bar{V}^0 \approx \left. \frac{\partial V}{\partial x_+^s} \right|_{\mathbf{x}_0} \bar{x}_+^s + \left. \frac{\partial V}{\partial x_-^s} \right|_{\mathbf{x}_0} \bar{x}_-^s + \left. \frac{\partial V}{\partial I} \right|_{\mathbf{x}_0} I. \quad (42)$$

The partial derivative of the voltage V with respect to the input current I evaluated at the reference point is given by

$$\left. \frac{\partial V}{\partial I} \right|_{\mathbf{x}_0} = \frac{2RT}{\mathcal{F}} \left(\frac{\theta_3}{\sqrt{(1-x_+^0)x_+^0} \sqrt{1+(\theta_3 I_0)^2}} - \frac{\theta_6}{\sqrt{(1-x_-^0)x_-^0} \sqrt{1+(\theta_6 I_0)^2}} \right). \quad (43)$$

which simplifies to

$$\left. \frac{\partial V}{\partial I} \right|_{\mathbf{x}_0} = \frac{2RT}{\mathcal{F}} \left(\frac{\theta_3}{\sqrt{(1-x_+^0)x_+^0}} - \frac{\theta_6}{\sqrt{(1-x_-^0)x_-^0}} \right) = -R_{ct}^0(\boldsymbol{\theta}) \quad (44)$$

when substituting for $I_0 = 0$. This term can be interpreted as a charge transfer resistance and will therefore be denoted R_{ct}^0 , resulting in the charge transfer voltage drop $\eta_{ct} = -R_{ct}^0 I$ in the voltage equation. The partial derivative with respect to the surface stoichiometry in the cathode and anode are given respectively by

$$\left. \frac{\partial V}{\partial x_+^s} \right|_{\mathbf{x}_0} = + \left. \frac{dU_+}{dx_+^s} \right|_{x_+^s=x_+^0} - I_0 \frac{RT}{\mathcal{F}} \frac{\theta_3 (1-2x_+^0)}{\sqrt{1+\frac{(\theta_3 I_0)^2}{(1-x_+^0)x_+^0}} ((1-x_+^0)x_+^0)^{3/2}} \quad (45)$$

and

$$\left. \frac{\partial V}{\partial x_-^s} \right|_{\mathbf{x}_0} = - \left. \frac{dU_-}{dx_-^s} \right|_{x_-^s=x_-^0} + I_0 \frac{RT}{\mathcal{F}} \frac{\theta_6 (1 - 2x_-^0)}{\sqrt{1 + \frac{(\theta_6 I_0)^2}{(1-x_-^0)x_-^0}} ((1-x_-^0)x_-^0)^{3/2}}. \quad (46)$$

Substituting for $I_0 = 0$ yields the simple expressions

$$\left. \frac{\partial V}{\partial x_+^s} \right|_{\mathbf{x}_0} = \left. \frac{dU_+}{dx_+^s} \right|_{x_+^s=x_+^0} = \alpha_+^0 \quad \text{and} \quad \left. \frac{\partial V}{\partial x_-^s} \right|_{\mathbf{x}_0} = - \left. \frac{dU_-}{dx_-^s} \right|_{x_-^s=x_-^0} = -\alpha_-^0 \quad (47)$$

where the α_i^0 denote the gradients of the open-circuit potential functions in each electrode, with respect to stoichiometry, at the linearisation point. Therefore, the linearised voltage measurement equation in the time domain becomes

$$\bar{V}(t) = \alpha_+^0 \bar{x}_+^s(t) - \alpha_-^0 \bar{x}_-^s(t) - R_{ct}^0(\boldsymbol{\theta}) I(t). \quad (48)$$

3.3. Transfer function of the linearised SPM

Taking the Laplace transform of the linearised voltage equation (48) and dividing by the input current I yields the transfer function of the linearised single particle model about the equilibrium point $\mathbf{x}_0 = (x_+^0, x_-^0, I_0 = 0)$

$$H^0(s, \boldsymbol{\theta}) = \frac{\bar{V}(s)}{I(s)} = \alpha_+^0 H_+^d(s, \boldsymbol{\theta}) - \alpha_-^0 H_-^d(s, \boldsymbol{\theta}) - R_{ct}^0(\boldsymbol{\theta}). \quad (49)$$

And substituting the anode and cathode diffusion transfer function H_+^d and H_-^d by their respective expressions (38) and (39) gives

$$H^0(s, \boldsymbol{\theta}) = \frac{\alpha_+^0 \theta_2 \tanh(\sqrt{s\theta_1})}{\tanh(\sqrt{s\theta_1}) - \sqrt{s\theta_1}} - \frac{\alpha_-^0 \theta_5 \tanh(\sqrt{s\theta_4})}{\tanh(\sqrt{s\theta_4}) - \sqrt{s\theta_4}} - R_{ct}^0(\boldsymbol{\theta}) \quad (50)$$

One can see that only the difference between the parameters θ_3 and θ_6 describing the cathode and anode kinetics appears in the charge transfer resistance term $R_{ct}(\boldsymbol{\theta})$ given by (44). As a result, there are clearly an infinite number of couples (θ_3, θ_6) that will yield the same transfer function and only the lumped parameter R_{ct} can be estimated using the linearised model at a given DoD. We have therefore reduced the parameter space to five parameters by combining the cathode and anode kinetics into the charge-transfer resistance term R_{ct} .

This is however assuming that the OCP slopes α_+^0 and α_-^0 are known parameters, but these are not directly measurable, since in practice, OCP is only able to be measured with respect to capacity (units Ah or Coulombs), not against stoichiometry (which is non-dimensional). By recognising that the theoretical capacity of an electrode is given by $Q_i^{th} = c_i^{max} \mathcal{F} V_i$ with $V_i = \epsilon A \delta_i$ (the volume of active material in the electrode), one can easily show that a variation of stoichiometry δx_i is proportional to a variation of charge/discharge capacity δQ according to

$$\delta x_i = \frac{\delta c_i}{c_i^{max}} = \frac{\delta c_i \mathcal{F} V_i}{Q_i^{th}} = \frac{\delta Q}{Q_i^{th}}. \quad (51)$$

Therefore the derivative of the OCP with respect to x_i can be related to its derivative with respect to charge/discharge capacity Q , denoted β_i^0 , according to

$$\beta_i^0 = \frac{\alpha_i}{Q_i^{th}} = \frac{1}{Q_i^{th}} \left. \frac{dU_i}{dx_i^s} \right|_{x_i^{s,0}} = \left. \frac{dU_i}{dQ} \right|_{x_i^{s,0}}. \quad (52)$$

Substituting α_i^0 for β_i^0 using (52) in (50) and recalling the expressions of Q_i^{th} in terms of θ_i in (26) yields the transfer function

$$H^0(s, \boldsymbol{\theta}) = \beta_+^0 f(s, \theta_1) - \beta_-^0 f(s, \theta_4) - R_{ct}^0 \quad (53)$$

where the function f defined as

$$f(s, \theta_i) = \frac{1}{3} \frac{\theta_i \tanh(\sqrt{s\theta_i})}{\tanh(\sqrt{s\theta_i}) - \sqrt{s\theta_i}}. \quad (54)$$

is only parametrised by the electrode diffusion time constant θ_1 or θ_4 in the cathode or anode respectively. The coefficients β_+^0 and β_-^0 are the measurable and assumed known OCP gradients with respect to capacity in the cathode and anode respectively. This requires access to half-cell or reference electrode cell data, which may be obtained from commercially available cells as we have recently demonstrated [28, 29]. In the absence of individual electrode OCP data, it is not possible to parameterise the SPM directly, although it may be reasonable to use a 2-electrode open-circuit voltage measurement combined with available OCP data from the literature for the graphite negative electrode to infer the positive electrode OCP function.

We have thus reduced the parameter estimation problem of the single-particle model to three independent parameters: the cathode diffusion time constant τ_+^d , the anode diffusion time constant τ_-^d and the charge-transfer resistance R_{ct} . We will subsequently define the vector $\tilde{\boldsymbol{\theta}} \in \mathbb{R}^3$ of parameters to be identified as

$$\tilde{\boldsymbol{\theta}} = [\tau_+^d \quad \tau_-^d \quad R_{ct}^0]^T. \quad (55)$$

The transfer function of the linearised SPM expressed in terms of the three parameters defined in $\tilde{\boldsymbol{\theta}}$ is given by

$$H^0(s, \tilde{\boldsymbol{\theta}}) = \beta_+^0 f(s, \tau_+^d) - \beta_-^0 f(s, \tau_-^d) - R_{ct}^0. \quad (56)$$

Figure 1 shows a Nyquist plot of the SPM frequency response predicted by (56) at 25% DoD for the LCO cell parameters given in table 1. At high frequencies, the response features a 45° slope which is representative of semi-infinite linear diffusion. This 45° slope is commonly referred to as the ‘diffusion tail’ in the battery electrochemical impedance spectroscopy (EIS) community and is usually modelled using a so-called Warburg constant-phase element [30, 31]. The cell frequency response tends towards a capacitive behaviour with decreasing frequency as exhibited by the vertical asymptote on the Nyquist plot. This capacitive

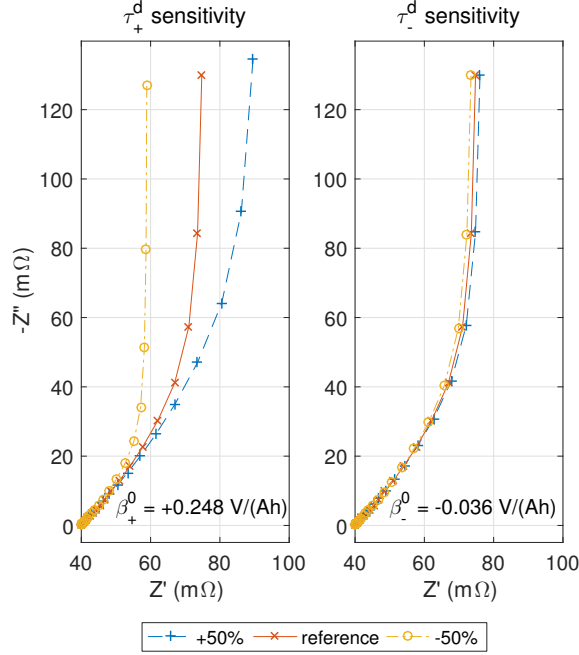


Figure 1: Comparison of the Nyquist frequency response predicted by the transfer function (56) using the reference parameters given in table 1 with (left) the cathode diffusion time constant τ_+^d and (right) the anode diffusion time constant τ_-^d varied by $\pm 50\%$ from their nominal values. The OCP slope values β_i^0 corresponding to the chosen linearisation point (DoD = 25%) are indicated on the graph for each electrode.

behaviour arises from the variation of the average particle concentration at low frequencies, as opposed to the surface concentration variation only, due to the finite-length nature of the diffusion problem. Although the low frequencies giving rise to this capacitive behaviour are usually avoided in the lithium-ion battery EIS literature, we argue that the departure from the semi-infinite diffusion 45° tail actually provides a more informative dataset for the parameter estimation of the SPM. Figure 1 also shows the effect of varying the diffusion time constant τ_+^d and τ_-^d in the cathode and anode respectively by $\pm 50\%$ from their nominal values. Generally, a larger diffusion time constant (slow diffusion) yields higher cell impedance as expected. Moreover a smaller diffusion time constant (faster diffusion) results in the capacitive behaviour occurring at higher frequencies; this is because faster diffusion results in easier variations of the average particle concentration. Finally, the frequency response is much more sensitive to the cathode diffusion than the anode diffusion because of the flat anode OCP curve at this DoD, as shown by the low value of the anode OCP slope β_-^0 compared to β_+^0 . This behaviour will be explained in more detail in the subsequent sections.

3.4. Structural identifiability analysis

Definition 1 of structural identifiability can now be applied to the SPM transfer function (56) parametrised by the three parameters in $\tilde{\theta}$. Following Definition 1, to check the

structural identifiability of the linearised model, we need to show that

$$\beta_+^0 f(s, \tau_+^d) - \beta_-^0 f(s, \tau_-^d) - R_{ct}^0 = \beta_+^0 f(s, \tau_+^{d*}) - \beta_-^0 f(s, \tau_-^{d*}) - R_{ct}^{0*} \quad \text{for almost all } s, \quad (57)$$

implies the parameters equality,

$$\begin{bmatrix} \tau_+^d & \tau_-^d & R_{ct}^0 \end{bmatrix}^T = \begin{bmatrix} \tau_+^{d*} & \tau_-^{d*} & R_{ct}^{0*} \end{bmatrix}^T. \quad (58)$$

Because the charge transfer resistance is the only additive term independent of s on both side of the equation, we clearly have that $R_{ct}^0 = R_{ct}^{0*}$ and the structural identifiability equation reduces to

$$\beta_+^0 f(s, \tau_+^d) - \beta_-^0 f(s, \tau_-^d) = \beta_+^0 f(s, \tau_+^{d*}) - \beta_-^0 f(s, \tau_-^{d*}) \quad \text{for almost all } s \quad (59)$$

Since f is a non-trivial function of the Laplace variable s , this equality holds in the general case for almost all s if and only if $\tau_+^d = \tau_+^{d*}$ and $\tau_-^d = \tau_-^{d*}$ and the linearised SPM is structurally identifiable. There are however a few cases where other solutions exist:

- If $\beta_+^0 = 0$ (resp. $\beta_-^0 = 0$), then any pair (τ_+^d, τ_+^{d*}) (resp. (τ_-^d, τ_-^{d*})) satisfy the identifiability equation and the linearised SPM becomes unidentifiable. This makes sense because a ‘flat’ open-circuit potential function hides any diffusion dynamics effect of that electrode as shown in Figure 1 for the anode diffusion when $|\beta_-^0| \ll |\beta_+^0|$.
- If the magnitudes of the open-circuit potential function in each electrode are equal $\beta_+^0 = -\beta_-^0 = \beta^0$, then interchanging the diffusion time constants $\tau_+^d = \tau_-^{d*}$ and $\tau_-^d = \tau_+^{d*}$ satisfies the structural identifiability equation, and the linearised SPM is structurally identifiable provided the diffusion time constants are ordered.

In conclusion, the linearised SPM is structurally identifiable in the general case. In practice the fact that a ‘flat’ open-circuit potential function results in unidentifiable parameters may not be as problematic as it sounds, since identification may be performed using data at several DoDs, ensuring the OCP functions have a significant slope in each electrode.

4. Frequency-domain parameter estimation

This section discusses the implementation of the estimation algorithm for the transfer function of the linearised SPM from frequency-domain EIS experimental data. The experimental set up is discussed in section 5.2.1. We define the vector $\boldsymbol{\theta}_{id}$ of parameters identified by the estimation algorithm in the general sense. Therefore, depending on the parameter estimation algorithm considered, $\boldsymbol{\theta}_{id}$ could be equal to the full vector of parameters $\boldsymbol{\theta}$ given by (25) or a subset of parameters such as $\tilde{\boldsymbol{\theta}}$ given by (55). The estimation is performed by finding the best fit in the least-squares sense, i.e. by minimising the sum of squared error between both the real and imaginary part of the experimental and predicted impedance at several frequencies. First, the loss function for the parameter estimation at a single DoD is presented and extended to the simultaneous estimation at several DoDs. Then, we show how the charge-transfer resistance R_{ct} at a given DoD can be estimated beforehand by simple linear regression.

4.1. Single DoD parameter estimation

The experimental electrochemical impedance of a cell at a given frequency ω_i is denoted by the complex number $Z_j(\omega_i) = Z'_j(\omega_i) + iZ''_j(\omega_i)$, where Z' and Z'' denote the real and imaginary part of the impedance respectively, and the subscript j denotes the DoD. Similarly, the impedance predicted by the SPM will be denoted $H_j(\omega_i, \boldsymbol{\theta}_{id})$ in the subsequent sections.

In the case where parameter estimation is performed on impedance data at a single DoD denoted by the subscript j , the algorithm minimises the loss function $L_j(\boldsymbol{\theta}_{id})$ defined as

$$L_j(\boldsymbol{\theta}_{id}) = \sum_{i=1}^{N_\omega} |Z_j(\omega_i) - H_j(\omega_i, \boldsymbol{\theta}_{id})|^2. \quad (60)$$

This loss function is the sum over N_ω chosen frequencies of the squared complex magnitude of the error between predicted and measured impedance. This is also equal to the sum of the squared real part and imaginary part error according to

$$L_j(\boldsymbol{\theta}_{id}) = \sum_{i=1}^{N_\omega} (Z'_j(\omega_i) - H'_j(\omega_i, \boldsymbol{\theta}_{id}))^2 + \sum_{i=1}^{N_\omega} (Z''_j(\omega_i) - H''_j(\omega_i, \boldsymbol{\theta}_{id}))^2. \quad (61)$$

The optimal parameter estimate in the least-squares (maximum likelihood) sense is therefore given by the estimator $\hat{\boldsymbol{\theta}}_{id}$ which minimises the loss function according to:

$$\hat{\boldsymbol{\theta}}_{id} = \arg \min_{\boldsymbol{\theta}_{id}} L_j(\boldsymbol{\theta}_{id}) = \sum_{i=1}^{N_\omega} |Z_j(\omega_i) - H_j(\omega_i, \boldsymbol{\theta}_{id})|^2 \quad (62)$$

4.2. Combined DoDs parameter estimation

As mentioned in section 3.4 and shown in section 5, the estimation of the parameter $\tilde{\boldsymbol{\theta}}$ based on the impedance data at a single DoD is unidentifiable in practice due to the flatness of one of the electrode open-circuit potential functions. Therefore, the parameter estimation must be performed against impedance measured at several DoDs. The loss function $L(\boldsymbol{\theta}_{id})$ in this case is simply defined as the sum of the loss functions L_j defined in (61) over N_{DoD} levels of DoD according to

$$L(\boldsymbol{\theta}_{id}) = \sum_{j=1}^{N_{DoD}} L_j(\boldsymbol{\theta}_{id}) = \sum_{j=1}^{N_{DoD}} \sum_{i=1}^{N_\omega} |Z_j(\omega_i) - H_j(\omega_i, \boldsymbol{\theta}_{id})|^2, \quad (63)$$

where j denotes the DoD. Again, the optimal parameter estimate is given by the argument $\hat{\boldsymbol{\theta}}_{id}$ minimising the loss function according to

$$\hat{\boldsymbol{\theta}}_{id} = \arg \min_{\boldsymbol{\theta}_{id}} L(\boldsymbol{\theta}_{id}) = \sum_{j=1}^{N_{DoD}} \sum_{i=1}^{N_\omega} |Z_j(\omega_i) - H_j(\omega_i, \boldsymbol{\theta}_{id})|^2. \quad (64)$$

4.3. Estimation of the charge-transfer resistance by linear regression

Although the simultaneous parameter estimation at several DoDs could in theory improve the identifiability of the estimation problem (assuming the diffusion parameters are not a function of DoD), it also adds N_{DoD} charge transfer resistances R_{ct}^0 to identify because of the dependency of R_{ct}^0 on stoichiometry (or equivalently DoD) in (44). The charge-transfer resistance R_{ct}^0 is an additive purely resistive term in the transfer function describing the cell impedance. Therefore, it only shifts the impedance response along the real-axis on the Nyquist plot. In order to reduce the parameter space to be explored, the charge-transfer resistance R_{ct}^0 can be estimated separately by simple linear regression and subtracted from the experimental frequency-response data. Recalling from section 3.3 that the semi-infinite diffusion-driven impedance at higher frequencies feature a characteristic 45° slope, the charge-transfer resistance can be estimated by fitting a 45° straight line to the experimental response at higher frequencies, and extrapolating to find the intercept of this with the real axis on the Nyquist diagram. We assume that any high-frequency data points of the experimental EIS where charge-transfer processes are dominant (charge-transfer semicircle), have been removed; only data points at frequencies where diffusion processes are dominant remain.

Denoting $x_i = Z'(\omega_i)$ and $y_i = -Z''(\omega_i)$ the real part and negative imaginary part respectively of the experimental impedance at frequency ω_i , the linear regression problem is

$$y_i = \beta_1 x_i + \beta_0. \quad (65)$$

The slope is set to 45° to represent the diffusion behaviour as discussed previously. Therefore $\beta_1 = 1$ is known and the regression problem consists of estimating β_0 only from the experimental data. The charge-transfer resistance is then determined by calculating the intercept of the linear regression with the real axis of the Nyquist plot according to $R_{ct}^0 = -\beta_0$. Defining the variable $\bar{y}_i = y_i - \beta_1 x_i$, the regression problem can be written:

$$\bar{y}_i = \beta_0. \quad (66)$$

This therefore constitutes an over-determined system of N_ω equations with the only unknown β_0 , which can be written

$$\bar{\mathbf{Y}} = \beta_0 \mathbf{1}, \quad (67)$$

where $\bar{\mathbf{Y}} = [\bar{y}_1, \dots, \bar{y}_{N_\omega}]^T \in \mathbb{R}^{N_\omega}$ is the vector containing the values of \bar{y}_i at the N_ω frequencies, and $\mathbf{1} \in \mathbb{R}^{N_\omega}$ is a vector of all ones of length N_ω . The value of β_0 can easily be determined in the least-squares sense by computing

$$\beta_0 = \mathbf{1}^\dagger \bar{\mathbf{Y}} = \frac{\mathbf{1}^T}{N_\omega} \bar{\mathbf{Y}} \quad (68)$$

where the superscript $\mathbf{1}^\dagger$ denotes the pseudo-inverse of the vector $\mathbf{1}$ which is simply equal to a row vector with all components equal to $1/N_\omega$. This linear regression must be performed only using the experimental data points in the frequency range where low-frequency capacitive effects are negligible. Therefore, low-frequency impedance data points must be

discarded in the experimental dataset to perform a meaningful regression. In practice this was achieved by performing the regression first on all data points, and then on a reduced dataset where the lowest frequency impedance data point was removed until the goodness-of-fit was satisfactory. The coefficient of determination R^2 was used as an indicator to assess the goodness-of-fit and a threshold value of 0.98 was chosen to stop the iterations.

5. Results and discussion

5.1. Parameter estimation using synthetic data

The parameter estimation algorithm was first tested against synthetic data generated using the linearised SPM with a known set of parameters for an LCO cell from the literature [10], which are summarised in table 1.

Table 1: Parameters used for generating synthetic electrochemical impedance data for an LCO cell reported in [10].

Parameter	Units	Anode	Cathode
Electrode thickness δ_i	μm	73.5	70.0
Particle radius R_i	μm	12.5	8.5
Active material volume fraction ϵ_i	-	0.4382	0.3000
Li diffusivity in active material D_i	$\text{m}^2 \text{s}^{-1}$	5.5×10^{-14}	1.0×10^{-11}
Reaction rate constant k_i	$\text{m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1}$	1.764×10^{-11}	6.667×10^{-11}
Max. active material concentration c_i^{max}	mol m^{-3}	30 555	51 555
Electrode surface concentration \mathcal{A}	cm^{-2}	982	982
Electrolyte concentration c_e	mol m^{-3}	1000	

Figure 2 shows contour plots of the natural logarithm of the loss function $L_j(\tilde{\theta})$, (61), at several DoDs for the synthetic data. It is assumed that the charge-transfer resistance R_{ct} is known for each DoD since, as previously explained, it can be identified separately by straightforward linear regression. Therefore the two parameters to be identified are the cathode and anode diffusion time constants τ_+^d and τ_-^d respectively. The coordinates of the minimum values of the natural logarithm of (61) on these contour plots represent the optimal parameter estimates in the least-squares sense as defined in (62). The two cases for which the linearised SPM is structurally unidentifiable, as discussed in section 3.4, can be witnessed by examining figure 2. Firstly, when the absolute value of the OCP functions are approximately equal in the cathode and anode, $\beta_+ \approx -\beta_-$, such as 75 % DoD, the loss function clearly shows two minima: one minimum corresponds to the actual parameters, while the other minimum happens when the anode and cathode diffusion time constants are interchanged. Moreover, even if the absolute values of the electrode OCP slopes β_+^0 and β_-^0 are distinct (e.g. 5 %, 25 % and 95 % on figure 2), the loss function still features two local minima, although barely visible due to the narrow loss function along one axis. Therefore, an ambiguity persists and the anode and cathode dynamics cannot be distinguished. A possible explanation for this ambiguity is that the measured voltage is the difference between the anode and cathode

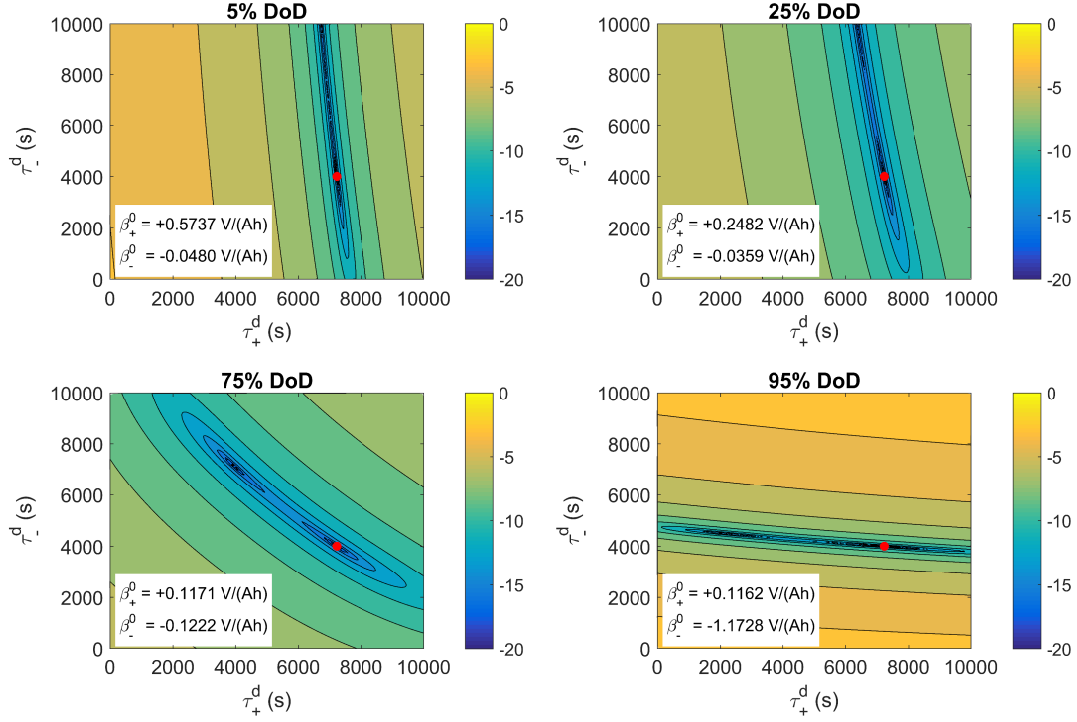


Figure 2: Contour plots of $\ln L_j(\tilde{\theta})$ against (τ_+^d, τ_-^d) at several DoDs assuming the charge-transfer resistance R_{ct} is known. Synthetic EIS data were generated using the linearised SPM with reference parameters found in the literature [10] for an LCO cell (shown as a red dot on the contour plot).

OCP and not the absolute voltage of the electrode with respect to a reference electrode. Secondly, in the case where one OCP slope is an order of magnitude lower in one electrode compared to the other, the diffusion time constant of this electrode becomes unidentifiable, e.g. 5 %, 25 % and 95 % DoD in figure 2. For instance at 95 % DoD, the absolute value of the cathode OCP slope β_+ is small compared to the anode one, and the minimum of the loss function is elongated along the τ_+^d axis, i.e. provided the value of τ_-^d is correct, almost any value for τ_+^d will result in a minimum value of the loss function.

These results suggest that the anode and cathode diffusion time constants cannot both be identified from frequency-data at a single DoD. In the best case where the OCP slopes are equal for the chosen DoD, the values τ_+^d and τ_-^d can be determined but cannot be assigned to a specific electrode. Figure 3 shows the natural logarithm of the loss function $L(\tilde{\theta})$ combining the EIS data at 5 %, 25 %, 75 % and 95 % DoD as defined in (63). This loss function shows a single global minimum corresponding to the actual set of parameters used to generate the synthetic data. The two time constants of the linearised SPM can therefore only be estimated unambiguously by considering EIS data at several DoDs. More specifically, complementary DoD values where each electrode in turn presents a large OCP slope while the other is negligible should be combined to ensure better identifiability. For instance, it is clear from figure 2 that combining EIS data at 5 % and 95 % DoD will result

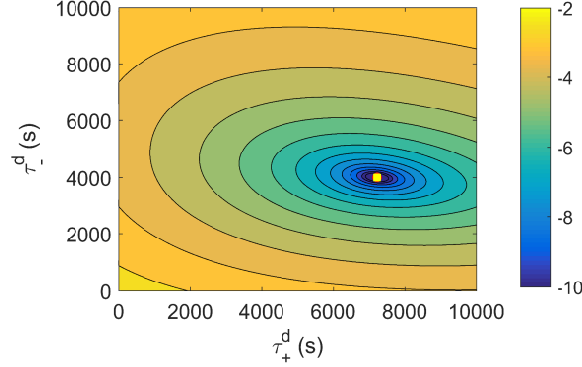


Figure 3: Contour plots of $\ln L(\tilde{\theta})$ against (τ_+^d, τ_-^d) assuming the charge-transfer resistance R_{ct} is known, based on synthetic EIS data with the reference parameters from [10] for an LCO cell (shown as a yellow square on the contour plot). The loss function is the sum of the cost function L_j for four levels of DoD 5 %, 25 %, 75 % and 95 %.

in a single minimum at the intersection of the lines of minimum loss function values for individual DoDs.

5.2. Parameter estimation using experimental data

This section discusses the results of the parameter estimation using EIS experimental data measured from a commercial Kokam NMC cell. First, the experimental procedure used to measure the cell impedance and the OCP for both electrodes is discussed. The estimation of the charge-transfer resistance using linear regression is then briefly considered. Finally, the practical identifiability of the model diffusion time constants from the experimental impedance data is examined.

5.2.1. Experimental setup

Electrochemical impedance spectroscopy experimental data were obtained for a Kokam SLPB533459H4 740 mA h NMC cell at several DoDs using a BioLogic SP-150 potentiostat. The cell was kept at a constant 20 °C temperature in a Vötsch VT4002 thermal chamber. The cell impedance was measured using single-sine Galvanostatic Electrochemical Impedance Spectroscopy (GEIS) with a peak-to-peak current amplitude of 100 mA and averaged over two periods. The impedance was measured at logarithmically-spaced frequencies with six frequencies per decade ranging from 5 kHz to 200 μHz. The EIS measurement using this experimental setup took approximately 9 hours for each DoD because of the low frequencies required. Clearly, the measurement of EIS at low frequency is quite time consuming and ultimately one should aim at using the minimum number of low-frequency data and/or DoD linearisation points to accelerate the model parametrisation. Figure 4 shows the measured EIS data as a Nyquist plot for several DoDs ranging from 10 % to 90 %. At high frequencies, the frequency response features a depressed semicircle, which is characteristic of charge-transfer processes. As discussed in section 4.3, this part of the plot is discarded because charge-transfer processes are approximated by the resistor R_{ct}^0 only in (56). As expected, in

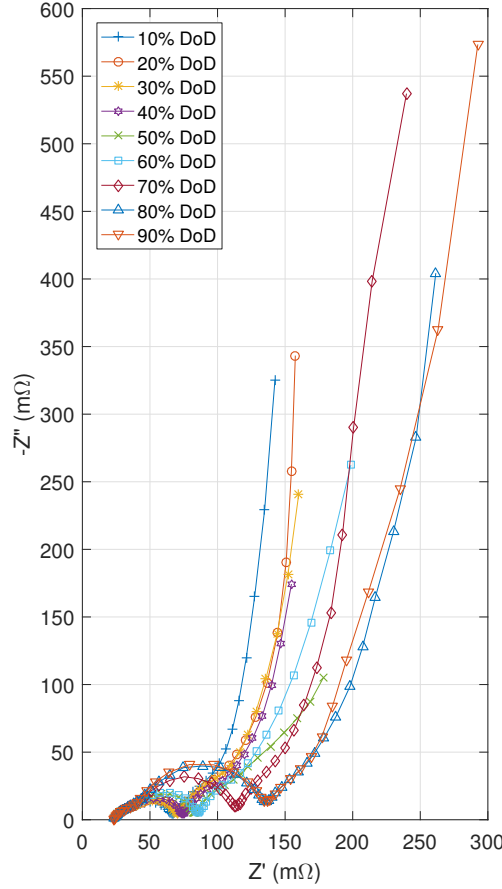


Figure 4: Nyquist plot of the electrochemical impedance of a Kokam SLPB 533459H4 740mAh NMC cell measured at 20°C and several DoDs in the frequency range 5 kHz to 200 μ Hz.

the medium range of frequency where semi-infinite diffusion is predominant, the frequency response shows the familiar 45° diffusion slope. At very low frequencies the response tends towards a capacitive vertical line due to the variations of the average particle stoichiometry.

Figure 6d shows the open-circuit potential of the Kokam SLPB533459H4 cell as a function of discharge capacity Q and DoD measured experimentally. In order to measure the anode and cathode potential separately, a minimally invasive reference electrode consisting of a lithium-coated copper wire was inserted into the commercial pouch cell using the technique presented in [29]. The OCV and the OCP of both electrodes were then measured using the galvanostatic intermittent titration technique (GITT) [28] by discharging the cell in 14.8mAh increments at $C/10$ and measuring the cell open-circuit voltage after a one-hour voltage relaxation time to obtain 50 measurements points.

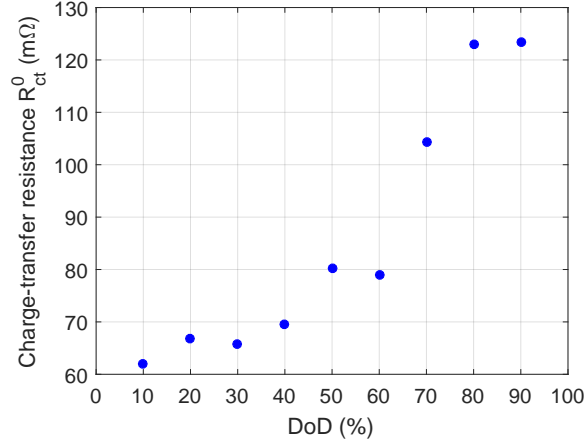


Figure 5: Charge-transfer resistance against DoD estimated from experimental data by linear regression.

5.2.2. Charge-transfer resistance estimation

The values of the charge-transfer resistance R_{ct}^0 estimated using the linear regression method discussed in section 4.3 as a function of DoD are reported on figure 5. Note that R_{ct}^0 as we have defined it actually includes the cell ohmic resistance, which is approximately 25 mΩ according to the intercept of experimentally measured impedance with the real-axis of the Nyquist plot at high frequencies, figure 4. As shown, the sum of the charge-transfer and ohmic resistances increases with DoD, which is consistent with previously reported Kokam NMC cell EIS data in the literature [32].

5.2.3. Parameter estimation performance

Figure 6 presents practical identifiability and parameter estimation results based on experimental impedance data at individual DoDs. Three characteristic values of DoD were chosen, 10 %, 50 % and 80 %, in order to demonstrate the identifiability issues discussed in section 3.4. At 10 % DoD only the cathode OCP shows a significant slope, at 50 % DoD both the cathode and anode OCP are flat, and at 80 % DoD both electrodes feature a significant OCP slope. The experimental and fitted impedance responses are shown on figure 6e, f and g for the chosen values of DoD. A satisfactory fit is obtained in all cases with a root-mean square error of 3.28 mΩ, 9.56 mΩ and 6.48 mΩ for 10 %, 50 % and 80 % DoD respectively.

However, the uncertainty on the parameter estimate is large as exhibited by the contour plots of the loss function on figure 6a, b and c. At 10 % DoD the loss function is very sensitive to the cathode diffusion dynamics while anode dynamics have very little impact because of the very small slope of the anode OCP. Therefore the estimated anode diffusion time constant τ_d^a is highly uncertain and cannot be estimated from this data set alone. In contrast, at 80 % DoD the loss function is sensitive to both the anode and cathode dynamics because of the similar magnitude of the OCP slope in both electrodes. However, the minimum of the loss function is still relatively elongated along the anode parameter axis, which suggests that the uncertainty on the anode parameter remains larger than the cathode one. This confirms that impedance data at several DoDs must be combined to yield less uncertain parameter

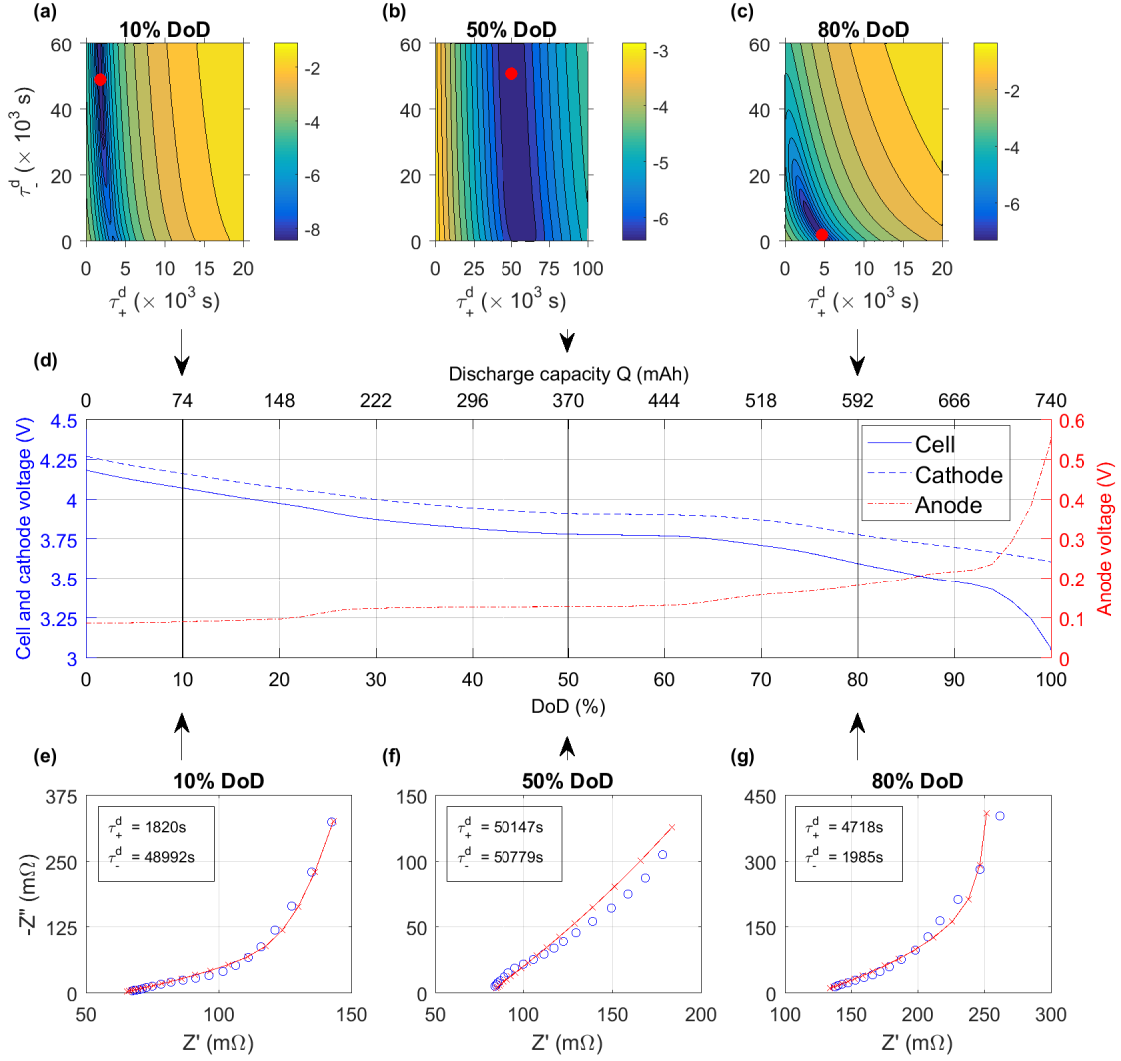


Figure 6: Natural logarithm of the individual DoD loss function $L_j(\hat{\theta})$ based on experimental EIS data at (a) 10%, (b) 50%, and (c) 80% DoD. (d) Cathode OCP, anode OCP and cell OCV of the Kokam cell as a function of DoD measured by the GITT technique using a minimally invasive reference electrode. Cell impedance experimentally measured (circles) and predicted (solid-lines and crosses) by the linearised SPM transfer function model fitted by minimising the individual DoD loss function $L_j(\hat{\theta})$ at (e) 10%, (f) 50%, and (g) 80% DoD.

estimates.

At 50% DoD, where the OCP is flat for both electrodes, the loss function is completely insensitive to the anode dynamics and somewhat more sensitive to the cathode dynamics. However, the contour plot of the loss function is actually shallow along the cathode parameter as well, which means that the uncertainty on both parameters is very large. Furthermore, the

minimum of the loss function happens for a cathode diffusion time constant centred around 60 000 s, figure 6b. This is approximately an order of magnitude higher than the value of τ_+^d estimated using the other data sets at 10 % and 80 % DoD. Throughout this work, the implicit assumption was made that both diffusion time constants do not vary with DoD. However, figure 6b suggests that lithium diffusivity in the electrode active material could drastically change with DoD. Experimental measurements of lithium diffusivities in the active material of a Kokam NMC cell are reported in [33] and confirm that lithium diffusivity can indeed vary by an order of magnitude depending on material lithiation. More especially, both the anode and cathode diffusivities are an order of magnitude lower around 50 % DoD compared to high DoDs for instance [33]. Furthermore, another source of uncertainty that has been ignored in the model is the error related to the OCP measurement and the calculation of the OCP slopes β_+^0 and β_-^0 . At 50 % DoD the OCP slopes in both electrodes are very small and therefore the relative error on measurement is large, especially considering that numerical differentiation is highly sensitive to noise. Finally, because of the flatness of the OCP slopes, both the anode and cathode diffusion dynamics have very limited effects on the cell terminal voltage at 50 % DoD. Therefore, the EIS data at 50 % DoD will be discarded from the parameter estimation using combined DoDs discussed subsequently.

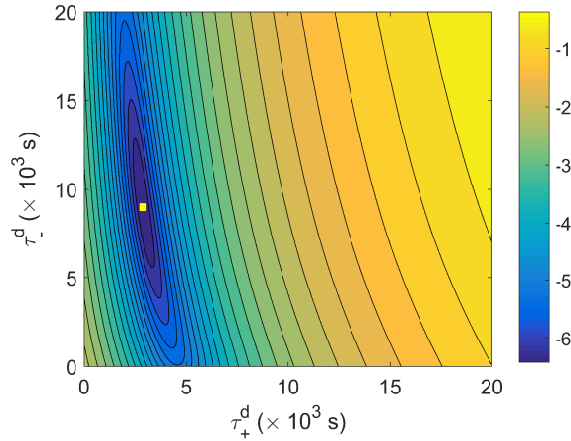


Figure 7: Contour plot of the loss function $\ln L(\tilde{\theta})$, (63), based on experimental impedance data at 10 % and 80 % DoD. The yellow square indicates the parameter estimated by the PE algorithm.

Figure 7 shows the contour plot of the cost function $L(\tilde{\theta})$ combining the experimental impedance data measured at 10 % and 80 % DoDs. Similarly to the results on synthetic data, figure 3, the loss function presents a single minimum, elongated along the anode parameter axis suggesting a larger uncertainty on the anode parameter compared to the cathode one. Although figure 7 suggests a ‘well-behaved’ estimation problem with a single parameter estimate, these results must be considered with caution. Indeed, the two combined datasets at 10 % and 80 % DoDs used to perform the parameter estimation were chosen somewhat arbitrarily. Although these parameter estimates yield a good impedance fit for these DoDs, it results in very approximate fitted impedance at other DoDs, e.g. 50 % DoD. Firstly, as previously mentioned the OCP slopes β_i in both electrodes are assumed fixed and perfectly

known for each DoD. The sensitivity of the predicted impedance response on the OCP slopes is not negligible. On the one hand, the computation of the OCP slope is highly sensitive to measurement noise because the measured voltage variations are relatively small between each DoDs, in the other order of a few millivolts. Further numerical errors are also introduced by interpolating between the 50 measurement points of the experimental OCP curves. Additionally, the measured OCP might not reflect closely enough the actual cell OCP. The OCP measurements were performed on a different cell (of the same type and size) which was modified by inserted a reference electrode. Although this technique is minimally invasive, it nonetheless may slightly modify the cell behaviour. Finally, electrode OCP is affected by temperature variation and hysteresis effects [28], which introduce further uncertainties. Secondly, our parameter estimation algorithm combining experimental data at several DoDs assumes that the diffusion time constants in both electrodes remain constant with DoD. Although solid-phase diffusivities are usually assumed constant with respect to active material lithiation in the lithium-ion battery electrochemical modelling community, e.g. [10, 12, 13, 34, 35], this assumption may introduce additional inaccuracies on the parameter estimate, especially for NMC cells [33]. All of these challenges provide fruitful avenues for further exploration.

6. Summary and conclusion

The analysis of parameter identifiability from experimental data is crucial prior to any attempt at estimating the parameters of battery first-principle models. We have demonstrated that the lithium-ion battery single particle model is over-parametrised and that only six subgroups of parameters are necessary to fully parametrise the model. Assuming that the open-circuit potential vs. discharge capacity curves for each electrode are known, we have shown that the estimation of the linearised single-particle model parameters at a given DoD can only identify three parameters among these six subgroups of parameters, namely the cathode diffusion time constant τ_+^d , the anode diffusion time constant τ_-^d and a charge-transfer resistance R_{ct} . Finally, we have shown the crucial role of the slope of electrode open-circuit potential curves on the parameter uncertainty. A flat electrode open-circuit potential curve results in high uncertainties on this electrode diffusion parameter. Therefore impedance data at a single DoD cannot, in general, result in accurate parameter estimation for both electrodes and experimental data at multiple DoDs must be considered. Specifically, complimentary DoDs where in turn the anode and cathode open-circuit potential gradients are significant must be chosen to yield satisfactory parameter identifiability. Future work will investigate the effects of temperature on the parameter estimation algorithm and the evolution of cell parameters with battery degradation.

Acknowledgements

This work was funded by Samsung Electronics Co. Ltd. through a collaborative research project between the Samsung Advanced Institute of Technology and the University of Oxford. We thank Dr Adam Mahdi (University of Oxford) for his valuable advice on the model

structural identifiability analysis, and Christoph Birkel (University of Oxford) for providing the experimental open-circuit potential data

References

- [1] R. Klein, N. A. Chaturvedi, J. Christensen, J. Ahmed, R. Findeisen, A. Kojic, State estimation of a reduced electrochemical model of a lithium-ion battery, in: American Control Conference (ACC), 2010, ISBN 9781424474271, 6618–6623, 2010.
- [2] S. J. Moura, N. A. Chaturvedi, M. Krstic, Constraint Management in Li-ion Batteries : A Modified Reference Governor Approach, American Control Conference (ACC), 2013 (2013) 5332–5337.
- [3] H. Perez, N. Shahmohammadhamedani, S. Moura, Enhanced Performance of Li-Ion Batteries via Modified Reference Governors and Electrochemical Models, IEEE/ASME Transactions on Mechatronics (2014) 1–10.
- [4] S. Santhanagopalan, R. E. White, Online estimation of the state of charge of a lithium ion cell, Journal of Power Sources 161 (2) (2006) 1346–1355, ISSN 03787753, doi:10.1016/j.jpowsour.2006.04.146, URL <http://linkinghub.elsevier.com/retrieve/pii/S0378775306008068>.
- [5] K. Smith, C. D. Rahn, C.-Y. Wang, Model-based electrochemical estimation of lithium-ion batteries, 2008 IEEE International Conference on Control Applications (1) (2008) 714–719, doi:10.1109/CCA.2008.4629589, URL <http://ieeexplore.ieee.org/lpdocs/epic03/wrapper.htm?arnumber=4629589>.
- [6] D. Di Domenico, A. Stefanopoulou, G. Fiengo, Lithium-Ion Battery State of Charge and Critical Surface Charge Estimation Using an Electrochemical Model-Based Extended Kalman Filter, Journal of Dynamic Systems, Measurement, and Control 132 (6) (2010) 061302, ISSN 00220434, doi:10.1115/1.4002475, URL <http://dynamicsystems.asmedigitalcollection.asme.org/article.aspx?articleid=1414570>.
- [7] K. Smith, C. D. Rahn, C.-Y. Wang, Model-Based Electrochemical Estimation and Constraint Management for Pulse Operation of Lithium Ion Batteries, IEEE Transactions on Control Systems Technology 18 (3) (2010) 654–663, ISSN 1063-6536, doi:10.1109/TCST.2009.2027023, URL <http://ieeexplore.ieee.org/lpdocs/epic03/wrapper.htm?arnumber=5256311>.
- [8] S. J. Moura, N. A. Chaturvedi, M. Krstić, Adaptive Partial Differential Equation Observer for Battery State-of-Charge/State-of-Health Estimation Via an Electrochemical Model, Journal of Dynamic Systems, Measurement, and Control 136 (1) (2013) 011015, ISSN 0022-0434, doi:10.1115/1.4024801, URL <http://dynamicsystems.asmedigitalcollection.asme.org/article.aspx?doi=10.1115/1.4024801>.
- [9] K. D. Stetzel, L. L. Aldrich, M. S. Trimboli, G. L. Plett, Electrochemical state and internal variables estimation using a reduced-order physics-based model of a lithium-ion cell and an extended Kalman filter, Journal of Power Sources 278 (2015) 490–505, ISSN 03787753, doi:10.1016/j.jpowsour.2014.11.135, URL <http://www.sciencedirect.com/science/article/pii/S0378775314020023>.
- [10] A. Bizeray, S. Zhao, S. Duncan, D. Howey, Lithium-ion battery thermal-electrochemical model-based state estimation using orthogonal collocation and a modified extended Kalman filter, Journal of Power Sources 296 (2015) 400–412, ISSN 03787753, doi:10.1016/j.jpowsour.2015.07.019, URL <http://linkinghub.elsevier.com/retrieve/pii/S0378775315300677>.
- [11] S. Zhao, A. M. Bizeray, S. R. Duncan, D. A. Howey, Performance evaluation of an extended Kalman filter for state estimation of a pseudo-2D thermal-electrochemical lithium-ion battery model, in: Proceedings of the ASME 2015 Dynamic Systems and Control Conference, 1–5, 2015.
- [12] P. W. C. Northrop, V. Ramadesigan, S. De, V. R. Subramanian, Coordinate Transformation, Orthogonal Collocation, Model Reformulation and Simulation of Electrochemical-Thermal Behavior of Lithium-Ion Battery Stacks, Journal of The Electrochemical Society 158 (12) (2011) A1461, ISSN 00134651, doi:10.1149/2.058112jes, URL <http://jes.ecsdl.org/cgi/doi/10.1149/2.058112jes>.
- [13] A. P. Schmidt, M. Bitzer, Á. W. Imre, L. Guzzella, Experiment-driven electrochemical modeling and systematic parameterization for a lithium-ion battery cell, Journal of Power Sources 195 (15) (2010) 5071–5080, ISSN 03787753, doi:10.1016/j.jpowsour.2010.02.029,

- URL <http://www.sciencedirect.com/science/article/pii/S0378775310002740>
<http://linkinghub.elsevier.com/retrieve/pii/S0378775310002740>.
- [14] V. Ramadesigan, K. Chen, N. a. Burns, V. Boovaragavan, R. D. Braatz, V. R. Subramanian, Parameter Estimation and Capacity Fade Analysis of Lithium-Ion Batteries Using Reformulated Models, *Journal of The Electrochemical Society* 158 (9) (2011) A1048, ISSN 00134651, doi:10.1149/1.3609926, URL <http://jes.ecsdl.org/cgi/doi/10.1149/1.3609926>.
 - [15] J. C. Forman, S. J. Moura, J. L. Stein, H. K. Fathy, Genetic parameter identification of the Doyle-Fuller-Newman model from experimental cycling of a LiFePO₄ battery, *Proceedings of the 2011 American Control Conference* (2011) 362–369 ISSN 0743-1619, doi:10.1109/ACC.2011.5991183.
 - [16] J. C. Forman, S. J. Moura, J. L. Stein, H. K. Fathy, Genetic identification and fisher identifiability analysis of the Doyle-Fuller-Newman model from experimental cycling of a LiFePO₄ cell, *Journal of Power Sources* 210 (2012) 263–275, ISSN 03787753, doi:10.1016/j.jpowsour.2012.03.009, URL <http://linkinghub.elsevier.com/retrieve/pii/S0378775312006088>.
 - [17] J. Marcicki, M. Canova, a. T. Conlisk, G. Rizzoni, Design and parametrization analysis of a reduced-order electrochemical model of graphite/LiFePO₄ cells for SOC/SOH estimation, *Journal of Power Sources* 237 (2013) 310–324, ISSN 03787753, doi:10.1016/j.jpowsour.2012.12.120, URL <http://dx.doi.org/10.1016/j.jpowsour.2012.12.120>.
 - [18] S. Jiang, A Parameter Identification Method for a Battery Equivalent Circuit Model, in: *SAE Technical Paper*, 2310, ISBN 0148-7191, 1–9, doi:10.4271/2011-01-1367, URL <http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:A+Parameter+Identification+Method+f>
<http://papers.sae.org/2011-01-1367/>, 2011.
 - [19] R. A. Nazer, V. Cattin, P. Granjon, M. Montaru, A new optimization algorithm for a li-ion battery equivalent electrical equivalent circuit identification., in: *9th International Conference of Modeling, Optimization and Simulation - MOSIM'12*, 2012.
 - [20] J. Jang, J. Yoo, Equivalent circuit evaluation method of lithium polymer battery using bode plot and numerical analysis, *IEEE Transactions on Energy Conversion* 26 (1) (2011) 290–298, ISSN 08858969, doi:10.1109/TEC.2010.2089796.
 - [21] N. Moubayed, J. Kouta, A. El-Ali, H. Dernayka, R. Outbib, Parameter identification of the lead-acid battery model, in: *2008 33rd IEEE Photovoltaic Specialists Conference*, ISBN 9781424416417, ISSN 0160-8371, 1–6, doi:10.1109/PVSC.2008.4922517, URL <http://ieeexplore.ieee.org/lpdocs/epic03/wrapper.htm?arnumber=4922517>, 2008.
 - [22] M. Doyle, T. F. Fuller, J. Newman, Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell, *Journal of The Electrochemical Society* 140 (6) (1993) 1526–1533, ISSN 00134651, doi:10.1149/1.2221597, URL <http://jes.ecsdl.org/cgi/doi/10.1149/1.2221597>.
 - [23] S. Atlung, K. West, T. Jacobsen, Dynamic aspects of solid solution cathodes for electrochemical power sources, *Journal of The Electrochemical Society* 126 (8) (1979) 1311–1321.
 - [24] G. Ning, B. N. Popov, Cycle Life Modeling of Lithium-Ion Batteries, *Journal of The Electrochemical Society* 151 (10) (2004) A1584, ISSN 00134651, doi:10.1149/1.1787631, URL <http://jes.ecsdl.org/cgi/doi/10.1149/1.1787631>.
 - [25] R. Bellman, K. J. ??str??m, On structural identifiability, *Mathematical Biosciences* 7 (3-4) (1970) 329–339, ISSN 00255564, doi:10.1016/0025-5564(70)90132-X.
 - [26] L. Ljung, *System Identification: Theory for the User*, Pearson Education, ISBN 9780132440530, 1998.
 - [27] S. M. M. Alavi, A. Mahdi, S. J. Payne, D. a. Howey, Structural identifiability of battery equivalent circuit models, *ArXiv e-prints* (2016) 1–18 URL <http://arxiv.org/abs/1505.00153>.
 - [28] C. R. Birkel, E. McTurk, M. R. Roberts, P. G. Bruce, D. A. Howey, A Parametric Open Circuit Voltage Model for Lithium Ion Batteries, *Journal of The Electrochemical Society* 162 (12) (2015) A2271–A2280, ISSN 0013-4651, doi:10.1149/2.0331512jes, URL <http://jes.ecsdl.org/content/162/12/A2271.abstract>.
 - [29] E. McTurk, C. R. Birkel, M. R. Roberts, D. A. Howey, P. G. Bruce, Minimally Invasive Insertion of Reference Electrodes into Commercial Lithium-Ion Pouch Cells, *ECS Electrochemistry Letters* 4 (12) (2015) A145–A147, ISSN 2162-8726, doi:10.1149/2.0081512eel, URL

- <http://eel.ecsdl.org/content/4/12/A145.abstract>.
- [30] E. Barsoukov, J. R. Macdonald, Impedance Spectroscopy, John Wiley & Sons, Inc., Hoboken, NJ, USA, ISBN 9780471716242, doi:10.1002/0471716243, URL <http://doi.wiley.com/10.1002/0471716243>, 2005.
 - [31] S. Buller, Impedance-based non-linear dynamic battery modeling for automotive applications, Journal of Power Sources 113 (2) (2003) 422–430, ISSN 03787753, doi:10.1016/S0378-7753(02)00558-X, URL <http://linkinghub.elsevier.com/retrieve/pii/S037877530200558X>.
 - [32] D. a. Howey, P. D. Mitcheson, V. Yufit, G. J. Offer, N. P. Brandon, Online measurement of battery impedance using motor controller excitation, IEEE Transactions on Vehicular Technology 63 (6) (2014) 2557–2566, ISSN 00189545, doi:10.1109/TVT.2013.2293597, URL <http://ieeexplore.ieee.org/lpdocs/epic03/wrapper.htm?arnumber=6678208>.
 - [33] M. Ecker, T. K. D. Tran, P. Dechent, S. Kabit, a. Warnecke, D. U. Sauer, Parameterization of a Physico-Chemical Model of a Lithium-Ion Battery: I. Determination of Parameters, Journal of the Electrochemical Society 162 (9) (2015) A1836–A1848, ISSN 0013-4651, doi:10.1149/2.0551509jes, URL <http://jes.ecsdl.org/cgi/doi/10.1149/2.0551509jes>.
 - [34] T. F. Fuller, M. Doyle, J. Newman, Simulation and Optimization of the Dual Lithium Ion Insertion Cell, Journal of The Electrochemical Society 141 (1) (1994) 1–10.
 - [35] M. Guo, G. Sikha, R. E. White, Single-Particle Model for a Lithium-Ion Cell: Thermal Behavior, Journal of The Electrochemical Society 158 (2) (2011) A122, ISSN 00134651, doi:10.1149/1.3521314, URL <http://jes.ecsdl.org/content/158/2/A122.full>.

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